

## Review Article

### Negative Thermal Expansion

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**Summary.** Materials with a negative thermal expansion coefficient contract when heated and expand when cooled. This paper reviews mechanisms of how this unusual property can be achieved at the molecular and macroscopic level. Some applications of this unusual property are also discussed.

**Keywords:** Negative thermal expansion, NTE, thermal contraction, zeolites

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#### Introduction

Many materials which we encounter in everyday life expand on heating. This fact of life is easily highlighted with a simple experiment that we are all familiar with and involves a metallic sphere passing through a metal ring. At room temperature, the sphere is of such a size that it can easily pass through the ring, but after the sphere is heated, it will have expanded with the result that it can no longer pass through the ring.

The phenomenon of thermal expansion may be explained by looking at interatomic distances. If we were to consider a crystal lattice close to absolute zero with individual atoms located next to each other in a regular pattern, the atoms would be vibrating to a relatively small extent, taking up a particular volume of space. As the temperature is increased, the atoms vibrate more and this corresponds to the material expanding as more volume is taken up by the vibrations.

Expansion in a material may be one of two forms: isotropic and anisotropic. In isotropic expansion, the material expands by the same extent in any direction (isotropically) upon heating. Polycrystalline aggregates and cubic materials undergo this form of expansion. In such cases, the extent of thermal expansion may be measured in terms of the volumetric thermal expansion coefficient  $\alpha_V$  which at constant pressure  $p$  is defined as follows:

$$\alpha_V = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad (1)$$

where  $V$  is the volume of the sample and  $T$  is the temperature. Alternatively, it may be expressed in terms of the density,  $\rho$ , through:

$$\alpha_V = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_p \quad (2)$$

However, not all materials expand in an isotropic fashion and instead, the extent of expansion will be dependent on the particular direction where the measurement is taken (i.e. anisotropic expansion). To quantify anisotropic

thermal expansion (e.g. in a generalised single crystal), it is more useful to define the thermal expansion in some particular crystallographic direction and in such cases, the linear expansion coefficient,  $\alpha_L$  is used. This is defined as:

$$\alpha_L = \frac{1}{L} \left( \frac{\partial L}{\partial T} \right)_p \quad (3a)$$

where  $L$  is the length of the unit cell in the direction of interest. This equation may be re-written in terms of  $\epsilon_L$ , the strain in the direction of measurement as follows:

$$\epsilon_L = \alpha_L dT \quad (3b)$$

or, more generally, for any direction, one may use the tensorial notation:

$$\epsilon_{ij} = \alpha_{ij} dT \quad i, j = 1, 2, 3 \quad (3c)$$

where  $\epsilon_{ij}$  are the elements of the strain tensor (i.e.  $\epsilon_{11}$ ,  $\epsilon_{22}$  and  $\epsilon_{33}$  are the strains in the  $Ox_1$ ,  $Ox_2$  and  $Ox_3$  directions respectively and  $\epsilon_{12} = \epsilon_{21}$ ,  $\epsilon_{13} = \epsilon_{31}$  and  $\epsilon_{23} = \epsilon_{32}$  are half the shear strains in the  $Ox_1$ - $Ox_2$ ,  $Ox_1$ - $Ox_3$  and  $Ox_2$ - $Ox_3$  planes respectively.

It should be noted that for isotropic systems which do not experience any shear,  $\alpha_{12} = \alpha_{13} = \alpha_{23} = 0$  whilst  $\alpha_{11} = \alpha_{22} = \alpha_{33} = \alpha_L$ . Also, in such cases,  $\alpha_V$  and  $\alpha_L$  are related through:

$$\alpha_L = \frac{\alpha_V}{3} \quad (4)$$

In most cases, materials expand when heated, i.e.,  $V$  increases ( $\rho$  decreases) or  $L$  increases as  $T$  increases with the result that thermal expansion coefficient  $\alpha_V$  or  $\alpha_L$  are positive (see equations (1) – (3)). However, it should be noted that materials which defy common expectation and contract when heated do exist, and in such cases, the thermal expansion coefficients assume a negative value. It should also be noted that for anisotropic systems, different values for  $\alpha_L$  may exist, depending on the direction of measurement. In fact, such materials may

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possess positive  $\alpha_L$ 's in one direction and zero or negative  $\alpha_L$ 's in other directions.

### Alternative forms for defining the thermal expansion coefficient

It is frequently the case that  $\alpha_V$  is expressed in other forms apart from the one in equation (1). For example, from the Maxwell relationship:

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \quad (5)$$

where  $S$  is the entropy of the system, from equations (1) and (5), the volumetric thermal expansion coefficient  $\alpha_V$  may also be written as:

$$\alpha_V = -\frac{1}{V} \left(\frac{\partial S}{\partial p}\right)_T \quad (6)$$

Also, defining the isothermal compressibility coefficient,  $\chi_T$  by:

$$\chi_T = -\frac{1}{K_T} = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \quad (7)$$

where  $K_T$  is the isothermal bulk modulus, then from equations (6) and (7):

$$\alpha_V = \chi_T \left(\frac{\partial S}{\partial V}\right)_T = -\frac{1}{K_T} \left(\frac{\partial S}{\partial V}\right)_T \quad (8)$$

Alternatively, using the Maxwell relationship:

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad (9)$$

then, for constant volume conditions,  $\alpha_V$  may be expressed as:

$$\alpha_V = \chi_T \left(\frac{\partial p}{\partial T}\right)_V = -\frac{1}{K_T} \left(\frac{\partial p}{\partial T}\right)_V \quad (10)$$

An important parameter when studying thermal expansion is the Grüneisen parameter  $\gamma$  (Grüneisen 1926). This parameter represents the thermal pressure from a collection of vibrating atoms and is defined as:

$$\gamma = \frac{V}{C_V} \left(\frac{\partial p}{\partial T}\right)_V \quad (11)$$

where  $C_V/V$  is the heat capacity per unit volume at constant volume. Thus, from equation (10), the volumetric thermal expansion coefficient  $\alpha_V$  may be written in terms of the Grüneisen parameter  $\gamma$  as follows:

$$\alpha_V = \frac{\chi_T C_V}{V} \gamma = \frac{C_V}{VK_T} \gamma \quad (12)$$

where  $\chi_T$  is the isothermal compressibility coefficient,  $K_T$  is the isothermal bulk modulus and  $C_V$  is heat capacity at constant volume. The Grüneisen parameter is dimensionless and its sign determines whether the expansivity is positive or negative.

Alternatively, for an adiabatic compression,  $\alpha_V$  may be written as:

$$\alpha_V = \frac{\chi_S C_p}{V} \gamma = \frac{C_p}{VK_S} \gamma \quad (13)$$

where  $C_p$  is heat capacity at constant pressure,  $\chi_S$  is the adiabatic compressibility coefficient and  $K_S$  is the adiabatic bulk modulus since these terms relate to the equivalent terms at constant temperature through:

$$\frac{K_S}{K_T} = \frac{\chi_T}{\chi_S} = \frac{C_p}{C_V} \quad (14)$$

and are defined through:

$$\chi_S = -\frac{1}{K_S} = V \left(\frac{dp}{dV}\right)_S \quad (15)$$

### Negative thermal expansion (NTE)

Although most materials exhibit positive thermal expansion, there are, in fact, some materials which exhibit negative thermal expansion (NTE) in some particular temperature range. When such materials experience an increase in temperature in their NTE range, they contract (i.e. shrink in size) with the result that their density increases.

NTE, is generally considered to be rare, unusual and limited to certain types of structures. Nevertheless, it is important to note that NTE has been shown to take place in a very common material: water. In fact, liquid water exhibits an increase in density between when heated between 273K and 277K whilst the hexagonal form of ice has a NTE coefficient at 45K (Rottger *et al.* 1994).

This review will provide information on some 'families' of materials which appear to possess NTE and discuss the main mechanisms which are responsible for this anomalous behaviour. Finally, the review will consider several applications which NTE materials have.

### Families of materials which undergo NTE

There are a number of classes of materials, in particular the  $ZrW_2O_8$  family of materials, the  $AM_2O_7$  family of materials and zeolites / zeolite-like materials. These systems have attracted considerable attention particularly due to the fact that their NTE window is unusually large (i.e. exhibit NTE over a large temperature range). These classes of materials are also of interest as members within the same class exhibit NTE windows with very similar or identical mechanisms occurring.

(i) *The  $ZrW_2O_8$  family*: Cubic zirconium tungstate ( $ZrW_2O_8$ ) (Evans *et al.* 1996; Evans *et al.* 1999a; Evans *et al.* 1999b) is the best known example of large isotropic negative expansion persisting over a wide temperature range. Although it is thermodynamically stable with respect to  $ZrO_2$  and  $WO_3$  only at high temperatures ( $\approx 1380$ – $1500$  K), it can be quenched and is then metastable from the lowest temperatures up to about 1050 K. Over all this range  $\alpha_V$  is negative. The crystal is cubic, with a rather complex structure (see Fig. 1) containing  $WO_4$  tetrahedra and  $ZrO_6$  octahedra which are linked in such a way that each  $ZrO_6$  unit shares its corners with six

different  $\text{WO}_4$  units, while each  $\text{WO}_4$  unit shares only three of its corners with  $\text{ZrO}_6$  units and the remaining oxygen in each  $\text{WO}_4$  tetrahedron is formally singly coordinated. Other materials in the  $\text{ZrW}_2\text{O}_8$  family which share the expansion properties include cubic  $\text{HfW}_2\text{O}_8$  (Evans *et al.* 1996; Mary *et al.* 1996),  $\text{ZrMo}_2\text{O}_8$  (Wilkinson *et al.* 1999; Allen & Evans 2003),  $\text{Zr}_{1-x}\text{Hf}_x\text{W}_2\text{O}_8$  and  $\text{ZrW}_{2-x}\text{Mo}_x\text{O}_8$  (Evans 1999); and  $\text{Zr}_{1-x}\text{M}_x\text{W}_2\text{O}_{8-y}$  ( $\text{M} = \text{Sc}, \text{In}, \text{Y}$ ) (Nakajima *et al.* 2002). All these systems have the same crystal structure as  $\text{ZrW}_2\text{O}_8$  and exhibit NTE over a wide temperature range. NTE in this family is well explained by invoking RUM (Rigid Unit Mode) models. In such cases, certain substructures within the unit remain at a fixed distance to each other and rotate as a whole. The mechanism is explained later on.

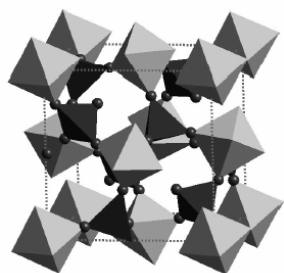


Figure 1. The structure of  $\text{ZrW}_2\text{O}_8$  at room temperature. The spheres represent oxygen atoms whilst the dark coloured tetrahedra are  $\text{WO}_4$ , whilst the light coloured octahedra represent  $\text{ZrO}_6$ . The rigid polyhedra are very clearly visible. The oxygen atoms act as hinges for these rigid polyhedral units. (Adapted from Barrera *et al.* 2005). The structure of  $\text{HfW}_2\text{O}_8$  is essentially similar, with Hf replacing Zr. The  $\text{ZrW}_2\text{Mo}_2\text{O}_8$  structure is also similar to that of  $\text{ZrW}_2\text{O}_8$  but it contains  $\text{MoO}_4$  units as well as  $\text{WO}_4$  units.

(ii) *The  $\text{AM}_2\text{O}_7$  family:* The  $\text{AM}_2\text{O}_7$  (e.g.  $\text{A} = \text{U}, \text{Th}, \text{Zr}, \text{Hf}, \text{Sn}$ ;  $\text{M} = \text{P}, \text{V}$ ) (Taylor 1984) phases are structurally closely related to  $\text{ZrW}_2\text{O}_8$  and form a second family of cubic materials which display isotropic negative thermal expansion under certain conditions (Korthuis *et al.* 1995; Koshrovani *et al.* 1996). This family is characterised by its distinctive structure which allows for a particular mechanism of NTE which is slightly different than in the case of the  $\text{ZrW}_2\text{O}_8$  family. In the  $\text{AM}_2\text{O}_7$  family, NTE arises from a deformation mechanism involving coupled 3D rotation of slightly distorted polyhedral units and non-linear M–O–M bridges. This is essentially a slight modification of the previously mentioned RUM mechanism.

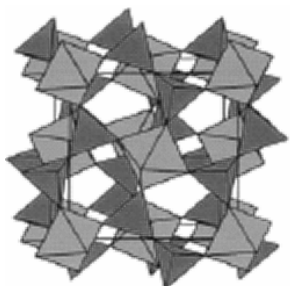


Figure 2: The structure of an  $\text{AM}_2\text{O}_7$  member. The large light gray polyhedra represent  $\text{M}_2\text{O}_7$  units while the smaller dark gray polyhedra represent  $\text{AO}_6$  units.

(iii) *Zeolites and zeolite-like materials:* A class of materials where NTE is quite frequent is that of zeolites and similar materials. The list of such materials includes siliceous FAU (Attfield and Sleight 1998), siliceous MWW, ITE and STT (Woodcock *et al.* 1999a), ISV, STF and MAPO-17 (Lightfoot *et al.* 2001), RHO (Bieniok & Hammonds 1998, Reisner *et al.* 2000, Lee *et al.* 2001), ERI (Attfield & Sleight 1998b, Tao and Sleight 2003b), siliceous CHA (Woodcock *et al.* 1999b), siliceous IFR (Villaescusa *et al.* 2001; Woodcock *et al.* 1999b) and calcined siliceous FER (Bull *et al.* 2003). A considerable number of these NTE cases are explained through RUMs (see below) but some studies have suggested reservations about these models (Tao and Sleight 2003a), particularly in the case of ERI (Tao and Sleight 2003b) where it has been suggested that the simpler ‘bridged transverse vibration’ mechanism (see below) is sufficient to explain some instances and also the fact that the RUM models must be modified to fit completely. A selection of these zeolites is shown in Fig 3.

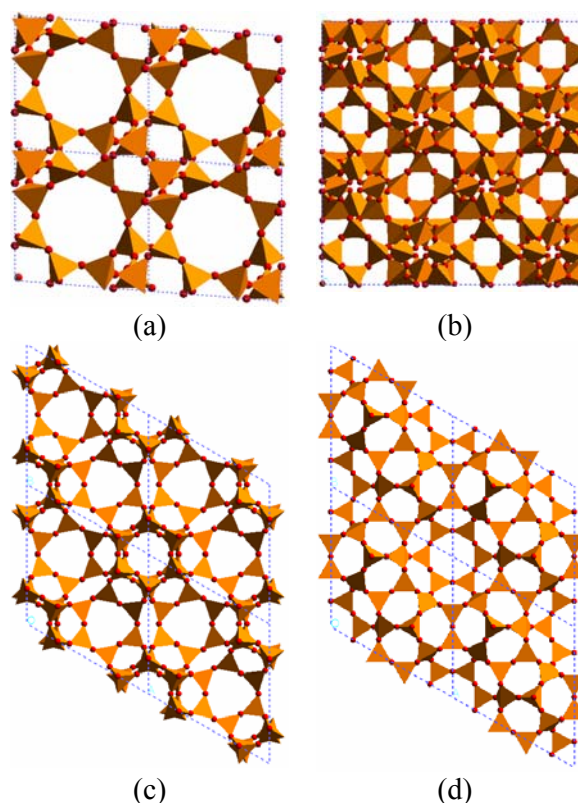


Figure 3: The polyhedral structures of (a) CHA and (b) FAU, (c) ERI and (d) MWW. In all cases the visualisation is in 2X2 cell format showing the (001) plane.

### Mechanisms resulting in negative thermal expansion

A number of mechanisms have been proposed to explain NTE in different materials. We now review the four principal mechanisms which all operate at the atomic scale and give rise to NTE in a wide range of materials.

Some less frequently occurring mechanisms will also be mentioned.

**(a) Mechanism 1: Shortening of bond lengths and phase changes**

Normally, as heat is applied to a structure, the bonds tend to lengthen and subsequently become weaker. However, there exist circumstances where solids which are about to undergo a phase change (to another solid state) exhibit certain changes in their atomic co-ordinates to the effect that certain bonds become stronger (shorter). This effect is usually the result of the formation of a less distorted crystalline system upon heating or the result of a rearrangement of the system as a consequence of a phase change.

NTE behaviour as a result of the formation of a more ordered system upon heating has been found to occur in  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$  where it is even more pronounced and similar perovskitic materials (Agrawal *et al.* 1987; Agrawal *et al.* 1988). In these systems, taking  $\text{BaTiO}_3$  as an example, one may observe that at room temperature, the  $\text{TiO}_6$  polyhedra are distorted (and thus the bonds are weaker and longer) but start to become more regular as heat is applied. This will result in a thermal contraction which occurs along the  $c$  crystal axis. This extent of thermal contraction is so pronounced that despite the fact that  $a$  and  $b$  vectors exhibit expansion, the net result is still a unit cell volumetric thermal contraction (i.e. negative  $\alpha_V$ ).

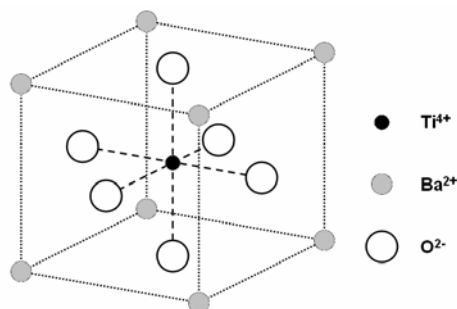


Figure 4: The idealised ‘crystal perovskite structure’ of  $\text{BaTiO}_3$ . The  $\text{TiO}_6$  tetrahedral units (i.e. the units with the O at the vertices and the Ti at the centre) illustrated in this figure are distorted at room temperature and become more regular as the temperature is increased, a process which results in a reduction in volume (i.e. NTE).

Once the phase shifts from the starting tetragonal state to the cubic phase, conventional thermal expansion once again starts to occur. Thus, the NTE mechanism occurs during the shift from the tetragonal to the cubic phase.

The phenomena of these bond length changes and phase changes are in fact closely related and it is often the case that the bond length changes may be the result of the solid in question undergoing a phase change. Sometimes, the NTE window is also associated with such a phase change. In such a case, as one heats the material, the

structure deforms and it may become conducive to contraction. For example, in some cases, reordering of species occurs within the lattice and this reordering is responsible for the NTE behaviour. Phase changes and NTE were correlated and studied in the cases of  $\text{ZrV}_{2-x}\text{P}_x\text{O}_7$  (Korthuis *et al.* 1995, see Fig. 2), lithium borates (Mathews *et al.* 1998),  $\text{ZrW}_2\text{O}_8$  (Yamamura *et al.* 2001, see Fig. 1) and related systems such as  $\text{HfW}_2\text{O}_8$  (Nakajima *et al.* 2002) and  $\text{ZrW}_2\text{Mo}_2\text{O}_{12}$  (Evans *et al.* 2000). Other studies involving NTE and phase changes were carried out by Ishii and co-workers (Ishii *et al.* 1999) who studied an ammoniated alkali fulleride compound which was reported to exhibit a phase change close to the NTE window whilst Tyagi *et al.* studied  $\text{A}_2(\text{MoO}_4)_3$  systems ( $\text{A} = \text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$ ) where the transition from the monoclinic to ortho-rhombic modification is accompanied by a large positive expansion followed by NTE. (Tyagi *et al.* 2002). Also, a phase change was reported to occur in  $\text{AgI}$  nanowires where the transition from the  $\beta$  to the  $\alpha$  form was found to be responsible for NTE in the temperature range 293 - 433K (Wang *et al.* 2003).

On the other hand, theoretical investigations by Christensen and co-workers (Christensen *et al.* 2000) regarding f.c.c. cesium suggest that negative thermal expansion is present but there is no isostructural transition.

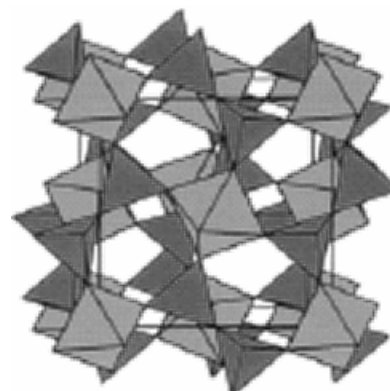


Figure 5: The structure of  $\text{ZrV}_{2-x}\text{P}_x\text{O}_7$ . The large light gray polyhedra represent  $\text{V}_{2-x}\text{P}_x\text{O}_7$  units while the smaller dark gray polyhedra represent  $\text{ZrO}_6$  units.

**(b) Mechanism 2: Bridging Atoms and RUMs**

Another important mechanism which results in NTE is that involving ‘bridging oxygens’, although it is important to note that the presence of ‘bridging oxygens’ does not automatically imply that the material exhibits NTE: the vast majority of systems containing bridging oxygens, do not, in fact possess the property of NTE.

NTE occurring via the ‘bridging oxygens’ mechanism can be explained by considering an M-O-M bond, (where M is usually a metal) which has an angle of  $180^\circ$ , where we may observe a thermal displacement for the bridging oxygen in the axis perpendicular to that of the bond. This



sideways motion which is shown in Fig. 6, will result in a decrease of the M-M distance. It has long been argued that such transverse vibrational modes (Barron 1957; Blackman 1957) can lead to NTE (White 1993).

This mechanism has been used to explain a NTE window between 25K and 573K for faujasite (FAU) (Attfield & Sleight 1998a). There have been reports of materials where the phenomenon takes place using the O-M-O configuration instead and examples include: cuprite  $\text{Cu}_2\text{O}$  (White *et al.* 1978; Schafer & Kirfel 2002),  $\text{Ag}_2\text{O}$  (Tiano *et al.* 2003; Beccara 2002) and  $\text{CuScO}_2$  (Li *et al.* 2002a). Li and co-workers (Li *et al.*, 2005) describe an experiment designed to understand the phenomenon and provide additional insight.

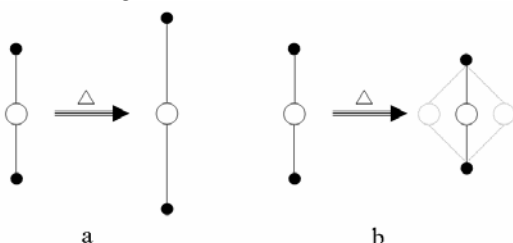


Figure 6. (a) A higher amplitude in atomic vibrations due to heat results in longer bond lengths which translates into a larger volume. In (b) the transverse vibratory-type motion of a species leads to reduction in the bond lengths (the dotted structures represent the extremal positions of the vibratory motions). The black and white spots represent species of different types.

Finally, the mechanism for NTE in  $\text{Zn}(\text{CN})_2$  (Williams 1997) has been described as being very similar with the CN group taking the role of the species performing the transverse thermal motion. An explanation for the NTE in gold cyanide ( $\text{AuCN}$ ) is also quite similar with species performing long wavelength motions perpendicular to the  $[\text{Au}(\text{CN})-\text{Au}(\text{CN})]$ -chain axis (Hibble *et al.* 2003).

For a material, there will be several different vibration modes at a given temperature and they may not all contribute to NTE. It has been postulated that transverse vibration modes are favoured at low temperatures and in fact several materials such as rubidium halides exhibit NTE at very low temperatures.

Interestingly, correlations can be made between the degree of covalency (rigidity) and the magnitude of the negative thermal expansion. This concept has been used to develop the RUM (or Rigid Unit Modes) (Giddy *et al.* 1993) and QRUM (Quasi RUM) models. The idea behind these models is actually a 'simple' model (Pryde *et al.* 1996) which considers polyhedra ( $\text{SiO}_4$ ,  $\text{WO}_4$ ,  $\text{ZrO}_6$ , etc.) linked at their corners by shared oxygens to be rigid. In this manner, large amplitude transverse vibrations of the oxygens can occur only through coupled oscillations of the tetrahedra and octahedra forming the structure. They involve no changes in intra-unit bond distances and angles, and so have relatively large amplitudes and low frequencies. The concept is illustrated in Fig. 7. It has also been used to explain NTE in calcined siliceous ferrierite (Bull *et al.* 2003), where it is suggested that tetrahedra oscillate *via* rigid modes of vibration.

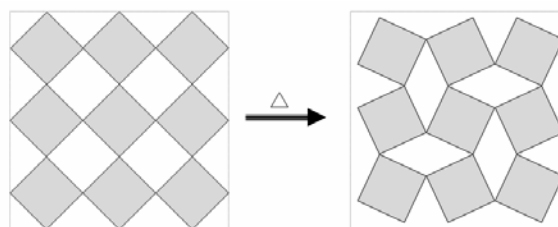


Figure 7. The RUM model involves a depiction of the structures as rotating squares where the sides of squares represent rigid bonds and the vertices represent flexible hinges (eg: shared oxygens). The dotted square represents the original area of this 2D RUM.

Detailed analysis is needed to find out whether a given structure can support RUMs and, if so, of what type. The RUM approach has been developed extensively by Dove, Heine and others (Giddy *et al.* 1993; Pryde *et al.* 1996; Pryde *et al.* 1998; Welche *et al.* 1998; Heine *et al.* 1999; Dove *et al.* 2000) and related to the standard Grüneisen theory. When there are many vibrations involving oscillations with only small distortions of the polyhedra, these are termed quasi-rigid unit modes (QRUMs), and can also give rise to negative expansion. A number of NTE materials have been explained through the use of RUM and QRUM models and these include:  $\text{ZrW}_2\text{O}_8$  (Pryde *et al.* 1998; David *et al.* 1999),  $\text{ZrV}_2\text{O}_7$ ,  $\text{AlPO}_4\text{-17}$  (Attfield & Sleight 1998b), various zeolite frameworks (Attfield & Sleight 1998a; Lightfoot *et al.* 2001; Bieniok & Hammonds 1998), beta-quartz (Welche *et al.* 1998), and  $\text{Sc}_2(\text{WO}_4)_3$  (Weller *et al.* 2000).

In recent years, questions have been raised regarding whether simple RUM models are sufficient to explain NTE in zirconium tungstate (Ravindran & Arora 2003; Cao *et al.* 2003). Ravindran and co-workers (Ravindran *et al.* 2001) claim that RUMs alone do not account for NTE in zirconium tungstate but one must consider also other phonons, including the bending modes of the  $\text{WO}_4$  group. The direct relationship between RUMs and NTE has also been challenged by Tao & Sleight (2003a) who cite several examples where NTE exists regardless of RUMs. The authors concede, however, that there is some form of correlation between the two. It has also been reported (Tao & Sleight 2003b) that the NTE that occurs in  $\text{AlPO}_4\text{-17}$  does not originate solely from RUMs but a very important contribution comes from other low-frequency vibration modes. The RUM model has also been described as insufficient for completely explaining the NTE in  $\text{Ag}_2\text{O}$  (Beccara 2002).

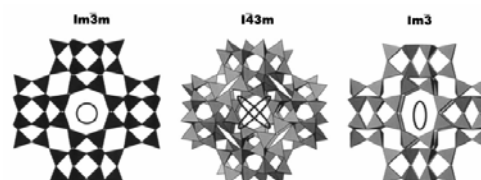


Figure 8. Rotations of rigid unit modes in the zeolite RHO framework type. The rotations are associated with phase transitions. (Adapted from Bieniok and Hammonds 1998).

The concept of RUMs is becoming increasingly popular for explaining NTE in many materials. Indeed, the RUM model is perhaps the easiest mechanism to understand from all those presented in this review, especially to the layman. However, while RUM models do provide a partial explanation of how NTE arises in the materials they are identified in, they fail to give a detailed view of why it arises, from the physical aspect. RUM models are also being used to investigate the intrinsic flexibility in framework structures and the effects that property has in structures and materials (Goodwin 2006).

### (c) Mechanism 3: Magnetostriction

Anomalous thermal expansion behaviour, including NTE has also been shown to exist in various cases of alloys and magnetic systems. Usually, for such systems, the NTE window occurs at low temperatures where vibrational contributions are small. In magnetostriction, what occurs is that in the wholly ordered ferromagnetic state the electron spins are aligned in parallel and are associated with a specific volume. The application of pressure to a state of partial ferromagnetic order causes the parallel spins to become less ordered, in turn contributing negatively to the thermal expansion (refer to Equation 6). This almost cancels the normal vibrational positive contributions, giving very low expansion or even negative expansion. At very low temperatures, the electrons are organised in domains which take up a certain volume. Upon heating, different energy levels for electrons become viable and when these are reached, the electronic configuration which is adopted is associated with a smaller volume, hence negative thermal expansion occurs.

Perhaps the most famous example of systems which exhibits anomalous thermal expansion behaviour is the ferromagnetic Invar<sup>†</sup> alloy  $\text{Co}_{0.65}\text{Ni}_{0.35}$  and alloys of similar composition (Guillaume 1897; Schlosse *et al.* 1971; Chikazumi 1979; Collocott & White 1986; Manosa 1991; Manosa 1992; Saunders *et al.* 1993; van Schilfgaarde *et al.* 1999; Kainuma 2002). Other systems which exhibit NTE include the orthorhombic antiferromagnetic  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$  (Harding *et al.* 1971),  $\text{CeNiSn}$  (Aliev *et al.* 1993) and the rare earth metal Holmium (White 1989). Materials such as  $\text{Lu}_2\text{Fe}_{17}$  and  $\text{Y}_2\text{Fe}_{17}$  have also been shown to exhibit negative thermal expansion below approximately 400 K (Gignoux *et al.* 1979). Tino and Iguchi (1983) investigated the possibility of NTE in Fe-Pd alloys and correlated the thermal expansion behaviour with that of Invar. The structure and magnetic properties of  $\text{Y}_2\text{Al}_3\text{Fe}_{14-x}\text{Mn}_x$  compounds (Hao *et al.* 2001) have been investigated by means of X-ray diffraction and NTE behaviour was found and attributed to magnetostriction.  $\text{Tb}_2\text{Fe}_{16}\text{Cr}$  (Hao *et al.* 2005a), thermoclinic perovskite  $\text{MnF}_3$  (Hunter *et al.* 2004) have also been shown to possess the property of NTE due to magnetostriction. Negative thermal expansion and spontaneous

magnetostriction of  $\text{Tb}_2\text{Fe}_{16.5}\text{Cr}_{0.5}$  (Hao *et al.* 2005b),  $\text{Dy}_2\text{AlFe}_{10}\text{Mn}_6$  (Hao *et al.* 2005c),  $\text{Dy}_2\text{AlFe}_{13}\text{Mn}_3$  (Hao *et al.* 2005d) and  $\text{Y}_2\text{Fe}_{16}\text{Al}$  (Hao *et al.* 2005e) have been documented.

The magnetic effects on NTE exhibiting molecule-based magnets  $\text{M}[\text{N}(\text{CN})_2]_2$  ( $\text{M} = \text{Co}, \text{Ni}$ ) (Kmetz *et al.* 1999) have also been investigated. For example, lanthanum manganite (Huang *et al.* 1997), which is another NTE material, has been studied with respect to magnetostriction. Also, a negative thermal expansion coefficient has been measured for b.c.c. Cr-Mn alloys (Shiga *et al.* 1986) and partly explained by magnetostriction.

### (d) Mechanism 4: Electronic effects

The volume of a system depends partly on the electronic configuration and changes in this configuration may lead to changes in the volume the system occupies. The volume of a material may in certain cases vary due to transfer of electrons, a transition which occurs at particular temperatures (e.g.: excitation of electrons to the previously unfilled conduction band). This volume change as a result of electron transfer does not necessarily result in NTE of the material; indeed below superconductive transition temperature, the positive expansion is enhanced; for Nb the expansion is decreased and at still lower temperatures becomes negative; and for Ta it is negative immediately below the transition temperature (White 1962).

The electronic configuration of a material may also become altered, such that the material has a NTE window which is associated with the availability of two different electronic configurations for a particular temperature window (Arvanitidis *et al.* 2003; Sleight 2003). When the material is heated, it may adopt a different electronic configuration which results in a decrease of the volume (see Fig. 9). This has been observed for samarium fulleride  $\text{Sm}_{2.72}\text{C}_{60}$  from 4.2 K up to 32 K, where there is an isosymmetric phase transition (Arvanitidis *et al.* 2003) and also in ytterbium fulleride (Margadonna *et al.* 2005) (see Fig. 10). This phenomenon is also thought to be responsible for negative thermal expansion below 60 K in  $\text{YbCuAl}$  (Mattens *et al.* 1980) and between 4.2 and 350 K in  $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$  (Mook and Holtzberg 1981), and for the approximately zero thermal expansion of the metallic compound  $\text{YbGaGe}$  (Salvador *et al.* 2003). The effect may also occur in pure metals: a fcc phase of Pr has  $\alpha \approx -20 \times 10^{-6} \text{ K}^{-1}$  between 550 and 700 K, attributed to electronic excitation from 4f to 5d (Kuznetsov *et al.* 2003). In the case of lanthanum manganite (Huang *et al.* 1997), the existence of different valence states of Mn and its possible relation to NTE in the material was also pointed out. NTE was also observed in  $\text{PrGaO}_3$  (see Fig. 10), and it can also be attributed to an interaction between the phonon vibrations and the electronic excitations of the Pr ion (Savytskii *et al.* 2003). Investigations carried out on b.c.c. Cr-Mn alloys (Shiga *et al.* 1986) indicate that the phenomenon may also be partly responsible for NTE

<sup>†</sup> The alloy INVAR is so called because its thermal expansion coefficient is approximately zero and therefore it has an invariable volume when subjected to changes in temperature.

in these materials. The phenomenon may also provide a partial explanation for the thermal contraction that occurs in gold nanoparticles at about 125K (Li *et al.* 2002b; Li *et al.* 2003).

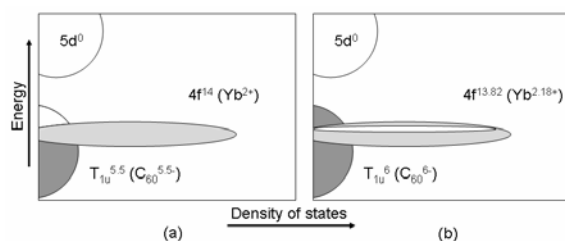


Figure 9: (a) This is a schematic diagram for the relevant electronic configuration of ytterbium fulleride at very low temperatures. (b) Upon heating (in the region of 60K), electron transfer from the 4f band of Yb to the  $T_{1u}$  band of the  $C_{60}$  occurs. This is accompanied by a change of the valence of Yb, such that the ionic radius decreases, (The diagram is adapted from [Margadonna \*et al.\* 2005](#)). The process, thus, results in NTE.

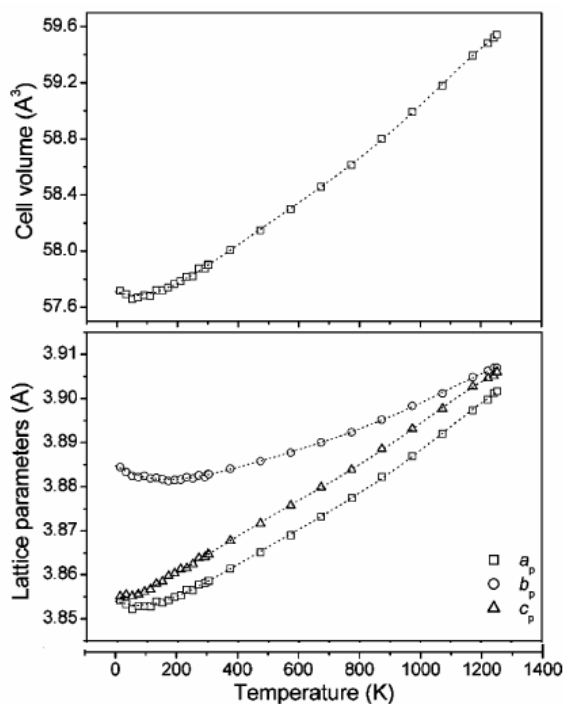


Figure 10: Measurements of the cell volume and parameters as they vary with temperature for  $\text{PrGaO}_3$ . (The measurements and graphs are taken from [Vasylechko \*et al.\* 2005](#)). The NTE window between circa 12K and 50K is evident.

An effect which is also involved in the mechanisms controlling thermal expansion and that can make them even more complex is that of superconductivity particularly at temperatures in the immediate vicinity of the superconducting transition. This is the case for the previous cited examples of Nb and Ta where cooling below the superconducting temperature results immediately in a negative thermal expansion coefficient for the latter while in the former case, the coefficient of thermal expansion decreases gradually until it becomes

negative. This expansion can also be strongly affected by the presence of magnetic fields. Such a case is illustrated in the investigations carried out on magnesium boride (Anshukova *et al.* 2003a; Anshukova *et al.* 2003b; Anshukova *et al.* 2003c).

‘Heavy fermionic’ materials (which are compounds where one of the constituent atoms has a partially filled 4f or 5f shell with high electron correlation) can present some of the most spectacular effects in thermal expansion in solids, especially at low temperatures (Ott *et al.* 1987). For example, the measured expansion  $\alpha_V$  of two different polycrystalline samples (Andres *et al.* 1975; Ribault *et al.* 1979) of the cubic material  $\text{CeAl}_3$  below 1K have been reported to be negative and very large. As regards  $\text{CeInCu}_2$  (de Visser *et al.* 1993) it was confirmed that the development of antiferromagnetic order in a strongly correlated electron system is correlated to a strong reduction of the coefficient of volume expansion, in accordance with decreasing hybridisation. The work of Aliev and co-workers (Aliev *et al.* 1993) on  $\text{CeNiSn}$  is also important to consider in this respect.

The behaviour of most heavy fermion materials is further complicated by anisotropy, and also by magnetic and superconducting transitions and thus it is highly dependent on the composition.

#### (e) Other mechanisms

There are other ‘mechanisms’ which result in NTE but do not relate to a class of systems. Quantum tunnelling is one such phenomenon. Tunnelling occurs for some substitutional impurities in alkali halides, and can give rise to either positive or negative thermal expansion. For example, replacement of the anion by 0.03%  $(\text{CN})^-$  in KBr causes the thermal expansion to become negative below 0.5 K, with a very large Grüneisen function of about  $-300$  at 0.1 K (Dobbs *et al.* 1986). In the case of systems where inter-molecular forces are weak, certain molecules in solids may sometimes behave as rotors. This may occur in the case of symmetrically equivalent H atoms, such as in  $\text{CH}_4$  (with different nuclear spin species), where investigations have yielded evidence of negative thermal expansion below 9K (Heberlein and Adams 1987). If the temperature in some systems is sufficiently low, the rotations may cease and the molecules oscillate at fixed orientations. This is the mechanism postulated for NTE in fulleride at and below 3.4K (Aleksandrovskii *et al.* 1997).

#### Applications

Materials exhibiting NTE are not only of interest due to the fact that this behaviour is highly anomalous, but also due to the fact that this anomalous behaviour can be exploited in many practical applications. For example,

- In the composites industry, where negative thermal expansion materials are used as components of composites to adjust the overall thermal expansion of composites to some particular value. The composite

- may be metal, polymer, or oxide-based. Predicting the thermal expansion of composites based on component properties is somewhat complex. Properties other than the thermal expansion of the components are important, in particular bulk or elastic moduli. It is interesting to note that a special system of carbon fibre composites and metals, with an extremely negative value of the thermal expansion coefficient, has been developed. The value is about three times that of steel, but with a negative sign. A further advantage of this system is its very low thermal conductivity and high compressive strength (Hartwig 1995).
- In the production of symmetric laminated beams with useful thermal deformation properties: Wetherhold & Wang (1995, 1996) suggest that by combining laminae having a positive coefficient of thermal expansion (henceforth referred to as CTE) with laminae having a negative CTE, one can control or tailor the laminate CTE and/or the laminate thermal curvature. The design of the beam can be naturally expressed in terms of property ratios and lamina thickness ratios. A three-layer beam offers one thickness ratio, and thus can be used either to control laminate CTE or eliminate thermal curvature. A five-layer beam offers two thickness ratios, and can be used to control the CTE and eliminate curvature.
  - In the construction of mechanically enhanced capillary columns through the deposition of  $\text{TiO}_2$ -doped silica (which has a negative thermal expansion coefficient) on the inside and outside of the silica tube results in the tube becoming compressed as it is heated, reducing the propagation of surface flaws (Berthou *et al.* 1993). Thus, NTE can be exploited in the design of surface-flaw-free tubes.
  - In the electronics area, there is a need for substrates and heat sinks that match the thermal expansion of Si. There are currently several active efforts in this area using  $\text{ZrW}_2\text{O}_8$  to reduce thermal expansion. In the heat sink application,  $\text{Cu}/\text{ZrW}_2\text{O}_8$  composites have been successfully made matching the thermal expansion of Si over at least a several hundred degree temperature range (Holzer & Dunand 1997).
  - In the production of ‘superior’ high field superconducting solenoid magnets: Such magnets sometimes quench by wire motion induced by electromagnetic force. It is suggested that the quick wire motions may be constrained by a high strength polyethylene fibre reinforced plastic (DFRP) bobbin with a negative thermal expansion coefficient and a low frictional coefficient (Yamanaka *et al.* 2002). Dyneema–glass hybrid composite fibre reinforced plastic (DGFRP) has negative thermal expansion, low frictional coefficient and high thermal conductivity and its use as material of a coil bobbin has also been described in literature (Takeo *et al.* 2003).
  - In the making of interfaces exhibiting good adhesion properties: It has been reported that additional reinforcing fibres with a negative thermal expansion coefficient such as Kevlar fibres are helpful to strengthen the reliability of the interface and enhance the actuating ability of SMA (shape memory alloy) hybrid composites (Zheng *et al.* 2005).
  - In medical applications: Another interesting application for NTE materials is that of adjusting the thermal expansion of the white composites used in teeth fillings. It is suggested that the thermal expansion of teeth and conventional fillings mismatch and this may result in failure (Versluis *et al.* 1996). Several groups working on such filling materials have been supplied with zirconium tungstate.
  - In the production of materials which do not change shape when heated: Zero thermal expansion is, of course, of profound interest. One of the biggest uses of such materials is as substrate materials for mirrors in various telescope and satellite applications (Collins and Richter 1995).
  - In the photonics sector, the use of NTE materials has been suggested in chirped fibre gratings (see Fig. 12). Wei and co-workers (Wei *et al.* 2001) theoretically analysed and experimentally demonstrated a simple method for adjusting the chirp of chirped fibre gratings by means of a temperature method, while the central wavelength is temperature insensitive. In this work, chirped fibre grating with tapered cross-section area was mounted under tension in a negative thermal-expansion coefficient material. Similar work has been carried out in this field by other workers including Mavoori *et al.* (1999) and Ngo *et al.* (2003), see (Fig. 11). Nishii *et al.* (2003) also report that channel waveguides with Bragg gratings have been fabricated on glass ceramic substrates with negative thermal expansion coefficient.

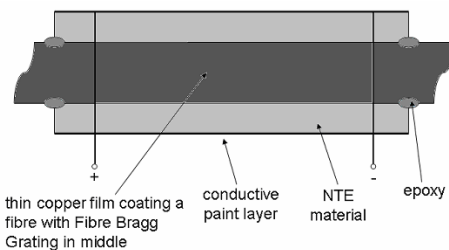


Figure 11: A schematic cross section representation of a Tunable Fibre Bragg Grating dispersion compensator, which involves a material with a NTEC encircling the coated fibre. (Diagram adapted from Ngo *et al.* 2003).



## Conclusions

In this review we gave an overview of existing work relating to materials exhibiting negative thermal expansion. The subject of NTE is by no means a new subject but there still exists much space for further work. In particular, the contribution to negative thermal expansion from certain electronic effects, especially at very low temperatures, is still not completely understood. Since a considerable number of NTE cases occur at very low temperatures, (and such conditions require huge efforts to bring about), it is evident that computer-based molecular modelling of such systems would be a valuable contribution to understanding how this counterintuitive behaviour arises. As computational power is constantly on the increase, quantum-based computer modelling of such systems will become more viable and as more information about this phenomenon becomes available, it is envisaged that a more complete picture of the phenomenon will emerge. Such research is also expected to yield a more extensive documentation of natural materials which possess this property. Furthermore, this useful property of NTE may in the future be engineered in structures as well as in synthetic materials, perhaps even resulting in the construction of structures and materials with tailor-made negative coefficients of thermal expansion at desired temperature ranges.

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